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Potentially toxic elements in muscle tissue of different fish species from the Sava River and risk assessment for consumers

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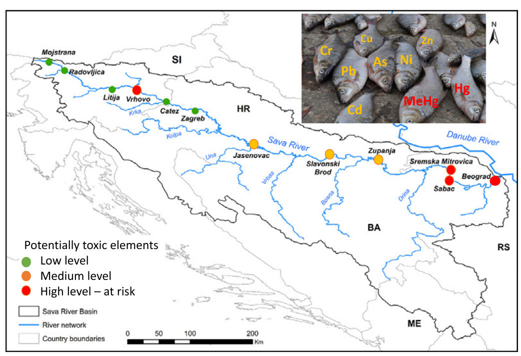
HIGHLIGHTS

- Potentially toxic elements determined in different fish species from Sava River.
- Potentially toxic elements concentrations were generally low, except for As and Hg.
- Concentrations of As and Hg in muscle tissue increases in the downstream direction.
- 90% of Hg was present in its most toxic form, namely MeHg.
- Estimated Daily Intake (EDI) for As and Hg exceeded Tolerable DI in the lower Sava

GRAPHICAL ABSTRACT



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ABSTRACT

Fish from the Sava River are consumed daily by the local people: therefore, concern has been raised about the health implications of eating contaminated fish. In the present study, potentially toxic elements (PTE), such as Zn, Cu, Cr, Ni, Cd, Pb, As, Hg, and methylmercury (MeHg), were determined in ichthyofauna that are commonly consumed. PTE were determined in the fish muscle tissue. Fish were sampled at 12 locations from the source of the Sava River to its confluence with the Danube River during two sampling campaigns, namely; in 2014 under high water conditions and in 2015 under normal water conditions. Due to the different water regimes, different fish species were collected for chemical analysis. We observed that the concentrations of elements analysed in the fish muscle tissue were generally very low, except for those of Hg. Moreover, more than 90% of Hg present in the fish was in its most toxic form, namely MeHg. Especially in fish from the 2015 sampling campaign, Hg and MeHg concentrations increased with fish size, trophic level, and in the downstream direction. In addition, for Pb and As, and to some extent for Cd and Cr, spatial differences were detected in both years. The highest concentrations of PTE were detected in fish from sites with intensive industrial and agricultural activities. The consumption of fish in general does not pose a health risk for the PTE studied, except for Hg/MeHg at selected contaminated sites.

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1. Introduction

In most aquatic habitats the concentrations of trace elements are low enough not to cause detectable effects on living organisms. In urbanised and industrialised areas this is not the case, as over time, the levels of trace elements in the aquatic environment increased as a consequence of urban runoff, agriculture, combustion of fossil fuels, cement production, mining, extractive metallurgy, pulp and paper production, etc. These listed activities are the main anthropogenic sources of most of the toxic trace elements (As, Cd, Cr, Cu, Zn, Ni, Pb, and Hg).

The concentration and the element species present in the water column as well as in sediments play an important role in determining metal bioavailability. On the other hand, the analysis of only water and sediment does not provide sufficient information about the effects that the elements present in these matrices have on the ecosystem. Therefore, the use of bioindicators is critical as they respond specifically to the bioavailable pollutants. Fish are considered to be good bioindicator organisms for the evaluation of aquatic environmental pollution by toxic elements (Chovanec et al., 2003; Lamas et al., 2007; Milošković et al., 2016). The level of element accumulation in fish is governed by abiotic factors such as nature and intensity of pollution, water pH, alkalinity and temperature, and biotic factors, such as size, age, feeding habits, and reproductive cycle (Milošković et al., 2016). Since different fish species accumulate and eliminate toxic elements in different ways, it is important to sample various fish species (Milošković et al., 2016). In order to distinguish recent from long-term exposure, fish of varying age (size) and from different trophic levels should be sampled (Dušek et al., 2005).

Cr, Cu, Fe, Se, Zn, Co and Mn in trace amounts are biologically essential for normal growth and functioning of fish, but at high concentrations they may cause adverse effects (Sfakianakis et al., 2015). As, Cd, Pb, Ni, and Hg are all nonessential elements and are highly toxic even at low levels (Varol and Sünbül, 2018). Some elements, such as Hg, can potentially accumulate and magnify along the food chain. Consequently, harmful concentration levels in higher trophic species may build-up. Regular human consumption of such fish may lead to serious adverse health effects (Varol and Sünbül, 2018). For the evaluation of the risk that consumption of contaminated fish poses to humans, different health risk estimation methods have been developed and used by numerous researchers (Yi et al., 2017; Griboff et al., 2017; Varol and Sünbül, 2018). One method is the Estimated Daily Intake (EDI), which helps to identify the quantity of pollutant consumed daily (Vrhovnik et al., 2013). The EDI of potentially toxic elements (PTE) depends on the concentrations of PTE in the food and the daily food consumption. In addition, human body weight has an important influence on the tolerance to contaminants (Vrhovnik et al., 2013).

The Sava River is the largest tributary to the Danube River. It is 945 km long and flows through Slovenia, Croatia, and Serbia, while its basin extends to Bosnia and Herzegovina and Montenegro. The Sava River is an important river on the Balkans that provides drinking water, water for irrigation, and fish for consumption. The upper stretches of the river are largely influenced by mineral weathering and hydromorphological pressures, while the middle is influenced by agricultural activities and, the lower stretches are affected mostly by industrial pollution and untreated municipal wastewaters (Komatina and Grošelj, 2015). Different parts of the Sava River have been studied in regard to contamination with inorganic pollutants such as PTE (As, Cr, Cu, Cd, Ni, Pb, Zn and Hg), over the years (Kotnik et al., 2003; Murko et al., 2010; Dragun et al., 2009; Sakan et al., 2016), but only two studies covered the entire course of the Sava River. The first was conducted during 2005 and 2006 (Milačič et al., 2010). In this study, it was found that the concentrations of PTE increased in the downstream direction, and that the Sava River was a moderately polluted European river with hotspots of Cr and Ni contamination in areas affected by metal and steel production industries and hotspots of Hg contamination in areas affected by chemical and chlor-alkali industries. The second study was conducted in 2014 and 2015 (Vidmar et al., 2017; Milačič et al., 2017a, 2017b). A trend of decreasing concentrations of PTE, especially in the sediments, was observed. Still, some hotspots of contamination with PTE, especially Hg, Cr, and Ni, were identified.

The content of PTE in water and sediments of the Sava River has been monitored, while scarce data regarding their impact on living organisms (such as fish) are available. Some studies have been conducted in restricted stretches of the Sava River on various fish species, as presented in Table 1, where a limited number of elements were reported. However, to the authors' knowledge there are no consistent studies on the concentrations of PTE in fish from different trophic levels over the entire course of the Sava River. As fish from the Sava River are consumed daily by the local people, concern has been raised about the health implications of eating contaminated fish. Consequently, the main objective of our study was to estimate how the presence of PTE in the aquatic environment is reflected in different fish species that are commonly fished for human consumption, and the extent of the risk to humans when consuming these fish. Therefore, the aims of our study were to determine the levels of PTE, such as Zn, Cu, Cr, Ni, Cd, Pb, As, Hg, and methylmercury (MeHg), and their potential for bioaccumulation/biomagnification; to evaluate possible correlations between the PTE present in the fish and those quantified in water and/or sediments from the same sampling locations that were published in Milačič et al. (2017b); and, as fish are an important constituent of the human diet, especially for the population inhabiting the lower stretches of the Sava River, to estimate the risk that consumption of these fish poses to humans by calculating the tolerable daily intake (TDI).

2. Materials and methods

2.1. Instrumentation

Analytical balance, Mettler AE 163 (Zürich, Switzerland), was used for all weighting. For freeze-drying of the samples Gamma 1-16 LSC plus Freeze-Dryer (CHRIST, Osterode am Harz, Germany) was used. A CEM Corporation (Matthews, NC, USA) CEM MARS 5 Microwave Acceleration Reaction System was used for digestion of the samples. PTE concentrations were determined by an Agilent Technologies (Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS), model 7700×. Concentration of Hg was determined by cold vapour atomic absorption spectrometry (CV AAS, Automatic Mercury Analyzer Model Hg-201, Sanso Seisakusho Co., LTD). Cold vapour atomic fluorescence detector (CV AFS) was used for MeHg concentration determinations (TEKRAN 2700, Toronto, Ontario, Canada).

2.2. Reagents

Ultrapure 18.2 MΩ cm water from a Direct-Q 5 Ultrapure water system (Merck-Millipore Watertown, MA, USA) was used. Suprapure nitric (65%) and hydrochloric (40%) acids, analytical grade sodium hydroxide, and perchloric (70%) and sulphuric (95–97%) acids were purchased from Merck (Darmstadt, Germany). Sodium tetraethyl borate (min 98%) was obtained from Strem Chemicals (Newburyport, Massachusetts, USA). A Stock ICP Multi Element Standard Solution XVI CertiPUR containing 100 mg/L $\pm$ 1 mg/L in 1.

mol/L HNO_3 was obtained from Merck. For the accuracy check DORM 4 Fish protein certified reference material (National Research Council Canada) was used.

2.3. Sampling and sampling sites

Two sampling campaigns were performed, first in September of 2014 under high water levels, and second in September of 2015 under low water level conditions. In 2015, the same sampling sites as in 2014 were chosen with one additional site in Mojstrana as a reference site. In total, 12 sampling sites were selected; Mojstrana (MOJ),